

Measurement of thermal expansivity and density as a function of pressure and study of isothermal compressibility and heat capacity

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Abstract

The main goal of this work was to verify the possibility of determining isothermal compressibilities as a function of pressure from density measurements by means of the Tait equation of state. It was also decided to calculate heat capacity. With this intention, thermal expansivities of decane, m-xylene and ethylbenzene were measured at 303.15 K and up to 300 bar with microcalorimetry as well as densities and speeds-of-sound of n-hexane, n-heptane, decane and cyclohexane at the same experimental conditions. Thermal expansivities and densities have been compared to literature data and calculated with the Tait equation as well. The calculation of isothermal compressibilities with the Tait equation showed that this method strongly depends on the determination of the parameters of the equation and the comparison with literature data was not sufficient to conclude on the cogency of this method. Heat capacities were estimated and it showed discrepancies up to 48% with literature data. Small variations of compressibilities had a major influence on this deviation. Thus, the Tait equation does not seem to be capable of determining appropriate isothermal compressibilities as a function of pressure.

Introduction

In a previous study [1], we have reported a set of experimental data about thermal expansivity of organic compounds in a range of pressures. In this continuing effort to provide data as a function of pressure, we report here results of experimental measurements of density and thermal expansivity at 303.15 K.

Density measurements were made with an Anton-Paar densimeter DMA 512 up to 300 bar at 303.15 K. Four compounds were studied: n-hexane, n-heptane, cyclohexane and decane.

Thermal expansivity was measured by calorimetry according to the scanning transitiometry method developed by Randzio [2]. Three new compounds were studied: decane, ethylbenzene and m-xylene.

These measurements will make it possible to estimate isothermal compressibilities with the Tait equation of state as well as heat capacities.

Experimental

Density measurements

The density was measured on an “Anton Paar Density Measurement System for Liquids and Gases type DMA 512” (for high pressures). A stainless steel cylindrical sample tube placed in a brass housing is maintained at a constant temperature by a thermostat liquid. Measurements can be performed in the temperature range 273.15 to 423.15 K and at pressures up to 400 bars.

The instrument constant was determined from calibration measurements on distilled water [3] and nitrogen [4].

The pressure was sustained by means of a high-pressure syringe pump (ISCO pump 260 D). The temperature is controlled by a thermostated bath and it is fixed at 303.15 K \pm 0.1K. The accuracy of the densimeter is $\pm 0.1 \text{ kg.m}^{-3}$.

Thermal expansivity measurements

Microcalorimetry was used here, according to the method developed by Randzio [2]. The experimental device and the method were described previously [1] so only a brief description will be done. An isothermal microcalorimeter LKB 2277 Bioactivity monitor, equipped with specially designed high-pressure cells, was used. The measuring cylinders are suspended in a 50-liter water bath, each cylinder containing metal heat sinks and a pair of measuring cells. The measuring cells operate in pairs, with one cell used as a reference and the other containing the sample. To exert the pressure in the sample cell, the fluid itself is used and the pressure is established by means of a high-pressure syringe pump (ISCO pump 260 D). The cell is filled at a constant flow with the compound under investigation so as to expel any air. After reaching thermal equilibrium, the fluid is pressurized while recording the heat evolution.

Thermal expansivity is determined with equation 2:

$$\left. \frac{dQ}{dt} \right|_T = (\alpha - \alpha_v) V T \frac{dP}{dt} \quad (1)$$

where Q is the heat released by the compression of the fluid, α the thermal expansivity of the fluid under investigation, α_v the thermal expansivity of the vessel (made of stainless steel 316 S), V the volume of the cell, T the temperature and P the pressure. The volume of the cell is $2.96 \text{ cm}^3 \pm 0.02 \text{ cm}^3$ and the thermal expansivity of the cell was evaluated to be $1.87 \times 10^{-5} \text{ K}^{-1}$. The latter value is within the broad range reported in the literature [5], [6], [7], [8].

The uncertainty of this method has been evaluated at 2 %.

Speed of sound

The measurements of speed of sound were performed previously [9], [10] in a specially designed high-pressure cell. The body of the cell consists of a jacketed chamber that

contains the sample. The temperature of the cell is controlled by a water bath. Piezoelectric transducers were used. Two transducers were placed on both sides of the cell, one to transmit a pulse and one to receive it. The transducer configuration that was used is a “through transmission” type and is more stable than a “pulse echo” one, where the pulse is transmitted from the transducer, reflected on a surface and received in the transducer again. The reliability of the equipment and the measurements was checked in [9] and the uncertainty has been evaluated to be 1.2 m.s⁻¹ for pure compounds.

Results and discussion

Density

The densities measured in this work were fitted to the Tait equation of state so as to avoid small irregularities. The Tait equation of state is described by the following equation:

$$\rho = \frac{\rho_0(T)}{1 - C(T) \ln \frac{B(T) + P}{B(T) + P_0}} \quad (2)$$

where $\rho_0(T)$ is the density at $P = P_0$, C and B are functions of temperature and P the pressure.

B and C follow the same equation:

$$B(T) = \sum_{i=1}^{N_c} b_i \frac{T - T_0}{100}^i \quad (3)$$

$$C(T) = \sum_{i=1}^{N_c} c_i \frac{T - T_0}{100}^i \quad (4)$$

The coefficients b_i and c_i are those taken from Cibulka et al. [11], [12], [13]. In these papers, Cibulka et al. critically reviewed experimental data and they give the parameters of the Tait equation.

Compounds	n-hexane	n-heptane	cyclohexane	decane
Coefficient B	544.89	610.21	708.65	797.14
Coefficient C (kg.m ⁻³)	0.103925	0.100472	0.093439	0.098479
Maximum deviation ^a (%)	0.23	0.12	-0.23	-0.47

a: deviation = (Density [Cibulka] – Density [this work]) / Density [Cibulka]

Table 1: Coefficients B and C of the Tait equation of state at 303.15 K and comparison with the densities provided by Cibulka et al. [11], [12]

The coefficients B and C were calculated in this work at 303.15 K, using the Microsoft Excel Solver, which uses the Generalized Reduced Gradient nonlinear optimization code. Table 1 gives these coefficients as well as the maximum deviation between the measured densities and the densities provided by Cibulka et al [11], [12]. Equation 1 requires the density at atmospheric pressure. The DIPPR correlation was used to calculate it. The maximum deviation reaches -0.47 % for the n-decane at 300 bar. It indicates that the apparatus allows accurate density measurements.

Thermal expansivity

Decane, ethylbenzene and m-xylene were studied and a comparison was made with literature data and with expansivity calculated from the Tait equation of state with equation 5:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (5)$$

Tables 2 to 4 present these results. Figure 1 compares the results to the literature data.

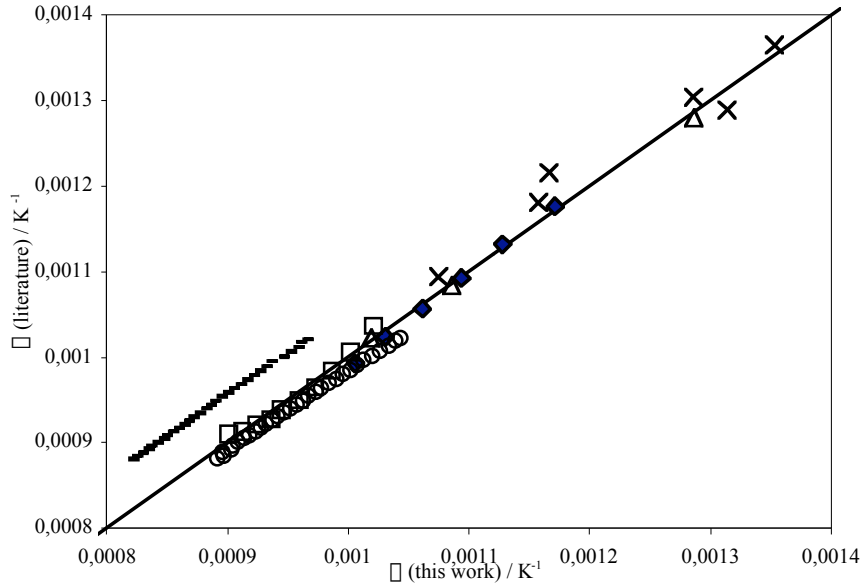


Figure 1: Thermal expansivity: comparison between literature and experimental data. Δ , n-heptane [1]; \square , decane [14]; \circ , toluene [1]; \times , n-hexane [1]; $*$, cyclohexane [1]; $-$, m-xylene [15].

The results from [1] were added in figure 1 to check if there were any systematic deviations due to our experimental device. One can see that the main deviation is reached with m-xylene (7% at 300 bar). Taravillo et al. [15] measured the density and then, from an equation of state, they calculated the isothermal compressibility and the thermal expansivity. Even though the deviations between their molar densities and literature data are always less than 0.2%, the deviation in isothermal compressibilities reaches 5%. The

equation of state may overestimate compressibility parameters and it could explain the deviation between this work and [15]

Figure 2 compares the results of this work to thermal expansivities calculated with the Tait equation of state [11], [12], [13]. The results of the previous work [1] were added in figure 2. The biggest deviation is obtained for cyclohexane (-9.9 % at 300 bar) but, for

the other compounds, the deviation does not have a regular behaviour: for decane, it varies between -1.1 and -0.5 %, for ethylbenzene between 2.8 and 4.5 and for m-xylene between -1.8 and 1.3 %.

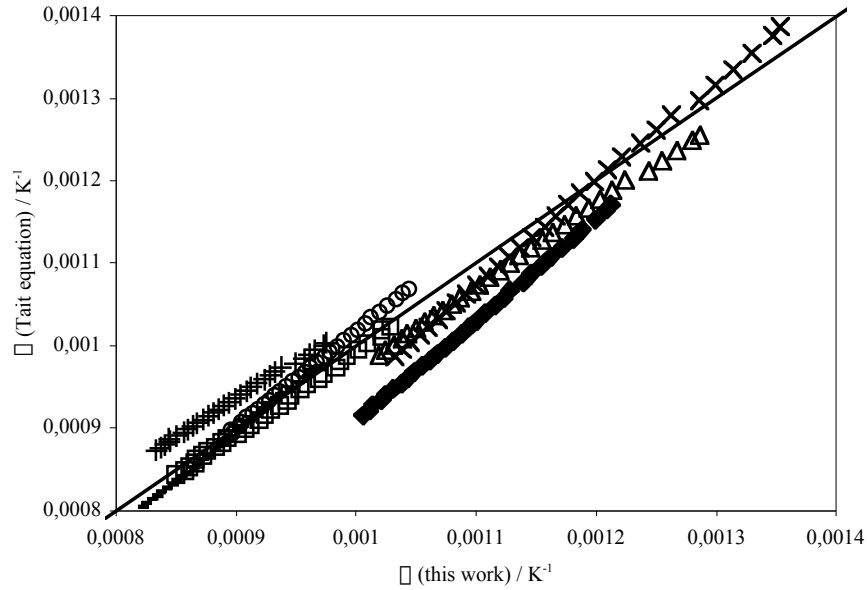


Figure 2: Thermal expansivity: comparison between literature and expansivity calculated with the Tait EOS. Δ , n-heptane [1]; \square , decane; \circ , toluene [1]; \times , n-hexane [1]; \diamond , cyclohexane [1]; —, m-xylene; +, ethylbenzene.

However, using the Tait equation of state does not appear to be accurate and this point is developed below.

The Tait equation: estimation of isothermal compressibility and heat capacity

A way of calculating isothermal expansivities is to measure density, to determine the coefficients required by the Tait equation and then to use equation 6:

$$\alpha_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T = \frac{C}{B+P} \cdot \frac{1}{1 + C \ln \left(\frac{B+P}{B+P_0} \right)} \quad (6)$$

This method was used in this work for four compounds: n-hexane, n-heptane, cyclohexane and n-decane. Figure 3 shows the comparison between compressibilities determined with the Tait equation of state from densities measured in this work and with the data given by Cibulka et al. [11], [12]. The deviations have quite dissimilar values: for n-heptane, it goes from -6.3 to -4.3 % and for n-hexane from 1.7 to 9.7 % for instance.

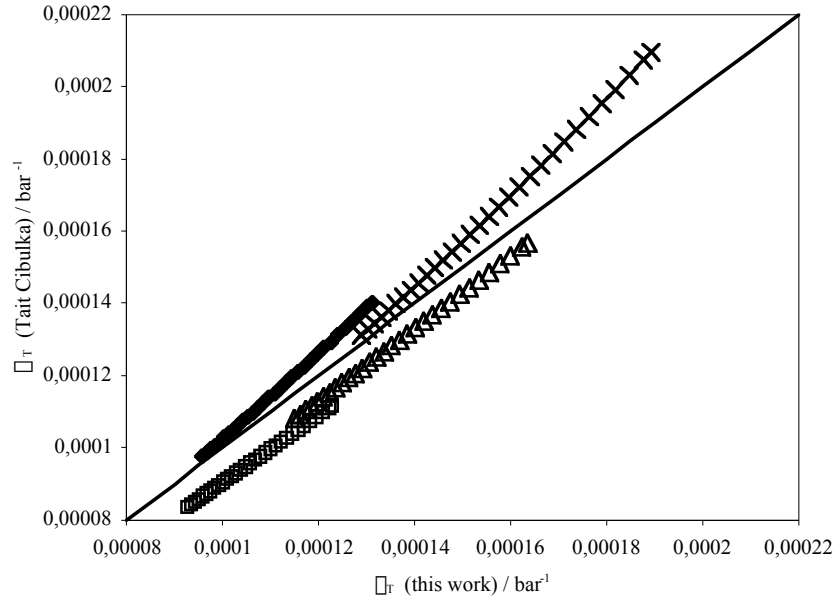


Figure 3: Isothermal compressibility: comparison between this work (with the Tait EOS) and literature data (Tait equation, [11], [12]). Δ , n-heptane; \square , decane; \times , n-hexane; \bullet , cyclohexane.

Compressibilities of cyclohexane and n-hexane are overestimated whereas the other ones are underestimated. The comparison with literature data [14], [16], [17] shows the same kind of discrepancies (figure 4).

The Tait equation describes density in a very accurate way but it does not seem to be relevant to calculate compressibility. These results were not sufficient to conclude on the capability of this method because the deviations are random. That is the reason why it was decided to determine heat capacity of these four compounds and to compare the results to literature data. Equation 7 was used for this purpose:

$$C_p = \frac{T\bar{\rho}^2}{\bar{\rho}\bar{\rho}_T\bar{\rho}\frac{1}{\bar{\rho}u^2}\bar{\rho}} \quad (7)$$

where C_p is the heat capacity ($\text{J.kg}^{-1}.\text{K}^{-1}$), $\bar{\rho}$ the density (kg.m^{-3}), $\bar{\rho}_T$ the thermal expansivity (K^{-1}), $\bar{\rho}$ the isothermal compressibility (Pa^{-1}), T the temperature (K^{-1}) and u the sound velocity (m.s^{-1}).

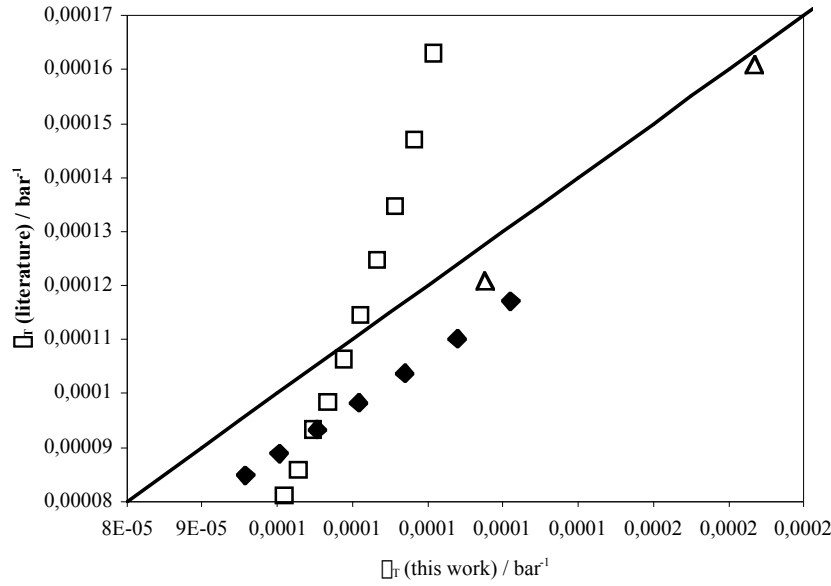


Figure 4: Isothermal compressibility: comparison between this work (from the Tait EOS) and literature data ([16], [17], [14]). Δ , n-heptane [16]; \blacklozenge , cyclohexane [17]; \square , decane [14].

Data of speeds of sound u [9], [10] will be published later but the present goal is to show a general behaviour of the heat capacity and not to focus on sound velocity. Thus, no more details will be given about the sound velocity data.

Heat capacities were calculated and the results were compared to literature data [16], [17], [18]. The deviation reaches 48 % for n-hexane and is at least about 20 %. The key factor is the compressibility. Small changes of β_T radically modify the values of heat capacity, as it is shown in table 5 for cyclohexane at 303.15 K.

P (bar)	C_p [literature] [17] (J.kg ⁻¹ .K ⁻¹)	with β_T [this work] (J.kg ⁻¹ .K ⁻¹)	D^a (%)	with β_T [Cibulka] [12] (J.kg ⁻¹ .K ⁻¹)	D^a (%)	with β_T [literature] [17] (J.kg ⁻¹ .K ⁻¹)	D^a (%)
50	1875.4	1294.55	31	1102.51	41	1945.98	-4
100	1866.9	1271.59	32	1110.63	40	1925.34	-3
150	1859.2	1258.25	32	1124.67	39	1911.44	-3
200	1852.3	1238.50	33	1130.65	39	1882.26	-2
250	1846.0	1214.15	34	1129.97	39	1840.22	0
300	1840.2	1196.75	35	1133.47	38	1807.40	2

a: $D = (C_p[\text{literature}] - C_p) / C_p[\text{literature}]$

Table 5: Heat capacities of cyclohexane as a function of pressure at 303.15 K according to different compressibilities.

The table above presents different values of heat capacity according to several compressibilities using equation 7. The deviation is about 30% with the compressibilities measured in this work, 40 % with compressibilities deduced from [12] and between -4 and 2% with compressibilities from [17]. The Tait equation does not seem to supply satisfactory values compared to experimental measurements of compressibilities (mainly from sound velocities).

This phenomenon may be observed in the literature as well. For instance, Randzio et al. [19] measured the density of 1-hexanol and calculated the coefficients of the Tait equation. The densities are quite close to the ones provided by Cibulka et al. [20]: the difference reaches -0.7% at the most (at 2633 bar). However, the compressibilities show large discrepancies: from 5.2% at 95 bar to -15.9% at 3430 bar.

The determination of the coefficients B and C is crucial but it strongly depends on the numerical resolution of the problem. So, a question arises: is it possible to determine accurate isothermal compressibilities through an equation of state?

Conclusion

Density measurements were made for four common compounds with a good accuracy (< 0.5 %) with an aim of estimating their isothermal compressibilities. Microcalorimetry was used to determine thermal expansivities of three new compounds and the comparison with literature results shows that the method gives accurate results. The brief study of the Tait equation has revealed its weakness and its limit to determine compressibility or expansivity that requires derivatives. This point is emphasized by the determination of the heat capacity and that showed the major influence of compressibility. Thus, direct measurements of isothermal compressibility seem to be more appropriate.

Literature

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Table 2: Thermal expansivity of decane at 303.15 K as a function of pressure and comparison with literature data [14] and the Tait equation of state [11].

P (bar)	$10^3 \alpha$ (K ⁻¹)	$10^3 \alpha_{\text{literature}}^b$ [14] (K ⁻¹)	Deviation ^a (%)	$10^3 \alpha_{\text{Tait}}$ [11] (K ⁻¹)	Deviation ^a (%)
5	1.029			1.023	-0.6%
10	1.021			1.019	-0.3%
20	1.021	1.037	1.5%	1.011	-1.0%
30	1.009			1.003	-0.6%
40	1.002	1.006	0.4%	0.995	-0.7%
50	0.993			0.988	-0.5%
60	0.987	0.984	-0.3%	0.981	-0.6%
70	0.984			0.974	-1.0%
80	0.973	0.965	-0.8%	0.967	-0.6%
90	0.969			0.960	-1.0%
100	0.959	0.950	-1.0%	0.953	-0.7%
110	0.953			0.947	-0.7%
120	0.945	0.939	-0.7%	0.940	-0.5%
130	0.943			0.934	-1.0%
140	0.936	0.927	-1.0%	0.928	-0.9%
150	0.929			0.922	-0.8%
160	0.924	0.921	-0.3%	0.916	-0.9%
170	0.920			0.910	-1.1%
180	0.912	0.913	0.1%	0.904	-0.9%
190	0.908			0.899	-1.0%
200	0.901	0.910	0.9%	0.893	-0.9%
210	0.893			0.888	-0.6%
220	0.889			0.882	-0.7%
230	0.883			0.877	-0.7%
240	0.876			0.872	-0.5%
250	0.872			0.867	-0.6%
260	0.866			0.862	-0.5%
270	0.866			0.857	-1.0%
280	0.861			0.853	-1.0%
290	0.858			0.848	-1.1%
300	0.850			0.843	-0.8%

a: deviation = (literature – this work) / literature

b: in [14], T = 313.15 K.

Table 3: Thermal expansivity of m-xylene at 303.15 K as a function of pressure and comparison with literature data [15] and the Tait equation of state [13].

P (bar)	$10^3 \alpha$ (K ⁻¹)	$10^3 \alpha_{\text{literature}}$ [15] (K ⁻¹)	Deviation ^a (%)	$10^3 \alpha_{\text{Tait}}$ [13] (K ⁻¹)	Deviation ^a (%)
5	0.963	1.021	5.6%	0.974	1.1%
10	0.958	1.018	5.9%	0.970	1.3%
20	0.956	1.012	5.6%	0.963	0.7%
30	0.949	1.006	5.6%	0.956	0.6%
40	0.944	1.001	5.7%	0.948	0.5%
50	0.934	0.995	6.2%	0.941	0.8%
60	0.929	0.990	6.1%	0.934	0.5%
70	0.924	0.984	6.1%	0.928	0.4%
80	0.920	0.979	6.1%	0.921	0.2%
90	0.914	0.974	6.2%	0.915	0.1%
100	0.908	0.969	6.2%	0.908	0.0%
110	0.903	0.964	6.3%	0.902	0.0%
120	0.897	0.959	6.4%	0.896	-0.1%
130	0.892	0.954	6.5%	0.890	-0.2%
140	0.887	0.949	6.6%	0.885	-0.3%
150	0.883	0.944	6.5%	0.879	-0.5%
160	0.880	0.940	6.4%	0.873	-0.7%
170	0.874	0.935	6.5%	0.868	-0.7%
180	0.869	0.930	6.6%	0.862	-0.8%
190	0.865	0.926	6.6%	0.857	-0.9%
200	0.862	0.922	6.5%	0.852	-1.1%
210	0.857	0.917	6.6%	0.847	-1.2%
220	0.852	0.913	6.7%	0.842	-1.2%
230	0.847	0.909	6.8%	0.837	-1.2%
240	0.844	0.905	6.7%	0.832	-1.5%
250	0.839	0.900	6.8%	0.827	-1.5%
260	0.834	0.896	7.0%	0.823	-1.4%
270	0.832	0.892	6.8%	0.818	-1.7%
280	0.827	0.888	6.9%	0.814	-1.6%
290	0.822	0.885	7.0%	0.809	-1.6%
300	0.819	0.881	7.0%	0.805	-1.8%

a: deviation = (literature – this work) / literature

Table 4: Thermal expansivity of ethylbenzene at 303.15 K as a function of pressure and comparison with the Tait equation of state [13].

P (bar)	$10^3 \alpha$ (K ⁻¹)	$10^3 \alpha_{\text{Tait [13]}}$ (K ⁻¹)	Deviation ^a (%)
5	0.976	1.003	2.8%
10	0.973	1.001	2.7%
20	0.966	0.995	2.9%
30	0.961	0.990	2.9%
40	0.957	0.984	2.8%
50	0.949	0.979	3.0%
60	0.938	0.974	3.7%
70	0.932	0.969	3.8%
80	0.929	0.964	3.7%
90	0.924	0.959	3.7%
100	0.918	0.954	3.9%
110	0.913	0.950	3.9%
120	0.909	0.945	3.8%
130	0.904	0.940	3.9%
140	0.899	0.936	3.9%
150	0.894	0.932	4.0%
160	0.890	0.927	4.1%
170	0.886	0.923	4.0%
180	0.881	0.919	4.1%
190	0.877	0.915	4.1%
200	0.873	0.911	4.1%
210	0.868	0.907	4.3%
220	0.864	0.903	4.3%
230	0.860	0.899	4.3%
240	0.857	0.895	4.3%
250	0.851	0.891	4.6%
260	0.844	0.887	4.8%
270	0.845	0.884	4.4%
280	0.841	0.880	4.4%
290	0.838	0.877	4.5%
300	0.834	0.873	4.5%

a: deviation = (literature – this work) / literature